

JCO9 Rec'd PCT/PTO 14 JUN 2001
09/868212

Atty. Docket #: 1998/F-135

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

INTERNATIONAL APPL. NO.: PCT/EP99/08830 :

INTERNATIONAL FILING DATE: -11/17/1999- :

APPLICANT: DIRK VANDERZANDE ET AL :

SERIAL NO: (To be assigned) : **ART UNIT:**

FILED: -HEREWITH- : **EXAMINER:**

FOR: "PROCESS FOR THE PREPARATION
OF DERIVATIVES
OF POLYARYLENEVINYLENE" :

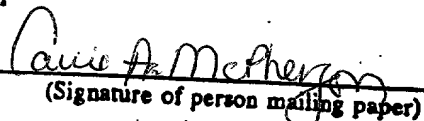
Commissioner for Patents
Box PCT
Washington, D.C. 20231

"Express Mail" No.: EK954159055

Date: - JUNE 14, 2001 -

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to the Commissioner for Patents, Washington, D.C. 20231

-Carrie A. McPherson-
(Typed or printed name of mailing paper or fee)


(Signature of person mailing paper)

**TRANSMITTAL OF APPLICATION PAPERS
TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. §371
(37 CFR 1.494 OR 1.495)**

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay.
4. ☒ A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2)) --
- a. ☒ is transmitted herewith (required when not transmitted by International Bureau).
 - b. ☐ has been transmitted by the International Bureau. See WIPO Publication WO 00/35987.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A (verified) translation of the International Application into the English language is enclosed.
7. ☐ Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
- a. ☐ are transmitted herewith (required if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has **NOT** expired.
 - d. ☐ have not been made and will not be made.
 - e. ☐ will be submitted with the appropriate surcharge.
8. ☐ A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371(c)(3)) is enclosed or will be submitted with the appropriate surcharge.

9. ☒ An oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371[c][4]) will follow.
[] and is attached to the translation of (or a copy of) the International Application.
[] and is attached to the substitute specification.

10. [] A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371[c][5]) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11. [] An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.

12. ☒ An Assignment for recording and a separate cover sheet in compliance with 37 CFR 3.28 and 3.31 will follow.

13. ☒ A FIRST preliminary amendment is enclosed.
A SECOND or SUBSEQUENT preliminary amendment is enclosed.

14. [] A substitute specification (including claims, abstract, drawing) is enclosed.

15. [] A change of power of attorney and/or address letter is enclosed.

16. ☒ Other items of information:

- ☒ This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of--

[] 22 months from the priority date under 37 CFR 1.494(c), or

☒ 32 months from the priority date under 37 CFR 1.495(c).

- ☒ The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

09/868212

JC18 Rec'd PCT/PTO 1 4 JUN 2001

International Application No. PCT/EP99/08830

1998/F-135

- ☒ Receiving Office: EPO
- ☒ IPEA (if filing under 37 CFR 1.495): EPO
- ☒ Priority Claim(s) (35 USC §§ 119, 365):
GERMAN Appln. 198 57 661.7 filed December 15, 1998.
- ☒ A copy of the International Search Report is
- ☐ enclosed.
- ☒ attached to the copy of the International Application.
- ☒ A copy of the Receiving Office Request Form is enclosed.
- ☒ Form PCT/IB/306 (1) sheet
- ☒ Form PCT/IB/308 (1) sheet
- ☒ Form PTO/SB/05 (1) sheet

The fee calculation is set forth on the next page of this Transmittal Letter.

FEE CALCULATION SHEET

☒ A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 860.00

Total Number of claims in
excess of (20) times \$18..... -0-

Number of independent claims
in excess of (3) times \$80..... -0-

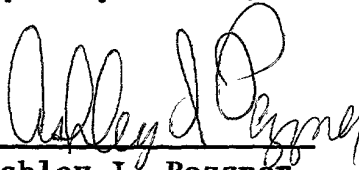
Fee for multiple dependent
claims \$270..... -0-

TOTAL FILING FEE... \$ 860.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By 

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1220 Market Street
P.O. Box 2207
Wilmington, Delaware 19899
Tel. (302) 658-9141

AIP/cam (8577*32)

Enclosures

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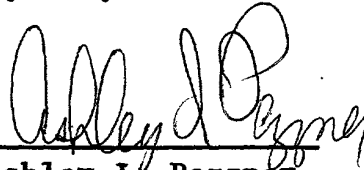
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: DIRK VANDERZANDE *ET AL.*)
SERIAL NO. TO BE ASSIGNED) ART UNIT: TO BE ASSIGNED
FILED: HEREWITH) EXAMINER: TO BE ASSIGNED
FOR: PROCESS FOR THE PREPARATION)
OF DERIVATIVES OF)
POLYARYLENEVINYLENE)

Asst. Commissioner for Patents
Washington, D.C. 20231

"EXPRESS MAIL" No. EK954159055 DATE: JUNE 14, 2001

I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231

CARRIE A. MCPHERSON
(TYPED OR PRINTED NAME OF
PERSON MAILING PAPER OR FEE)

Carrie A. McPherson
(SIGNATURE OF PERSON MAILING
PAPER OR FEE)

PRELIMINARY AMENDMENT

Sir:

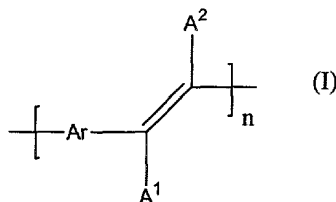
Prior to fee calculation and examination please amend the above-identified application as follows.

In the Claims

Please cancel claims 1-5.

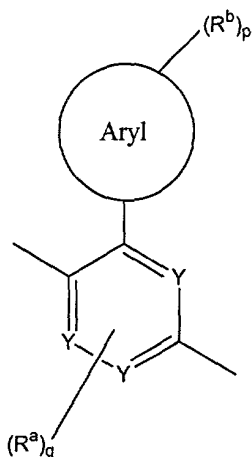
Please add the following new claims.

- -6. A process for the preparation of polymers of the formula (I)



in which Ar is Ar¹ or Ar² and

Ar¹ is an aromatic ring system having 4 to 20 carbon atoms, which is optionally monosubstituted or polysubstituted by C₁-C₂₀-alkyl, C₁-C₂₀-alkoxy, C₃-C₂₀-branched alkyl, phenyl or benzyl radicals and which further optionally contains up to 4 heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen in the aromatic ring system, is a radical of the formula



in which

Y are identical or different and are CH or N;

Aryl is an aryl group having 4 to 14 carbon atoms;

R^a and R^b are identical or different and are a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more non-adjacent CH₂ groups is optionally replaced by -O-, -S-, -CO-, -COO-, -O-CO-, -NR¹-, -(NR²R³)⁺-A⁻ or -CONR⁴- and in which one or more H atoms is optionally replaced by F, or are CN, F, Cl or an aryl group having 4 to 14 carbon atoms, which is optionally substituted by one or more non-aromatic radicals R^a;

R¹, R², R³ and R⁴ are identical or different and are aliphatic or aromatic hydrocarbon radicals having 1 to 20 carbon atoms or are alternatively H;

A^- is a singly charged anion or an equivalent thereof;

q is 0, 1 or 2;

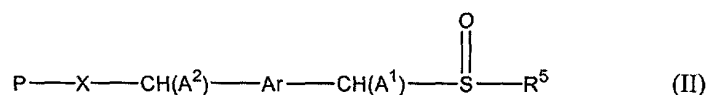
p is 1, 2, 3, 4 or 5;

A^1 and A^2 are identical or different and are hydrogen or a C_1 - to C_{20} - carbon-containing group; and

n is from 5 to 50,000;

which comprises the steps of

a) reacting at least one monomer of the formula (II)



in which

X is a leaving group, and

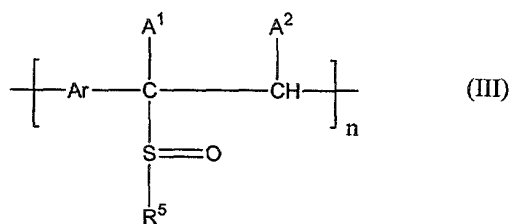
R^5 is unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl or C_1 - C_4 -alkyl-substituted cyclic alkyl, which is optionally substituted or unsubstituted and/or contain heteroatoms, such as O, N and Si,

P represents para in respect of the two methylene radicals $-CH(A^1)-$ and $-CH(A^2)-$ on both sides of the radical Ar ,

in which Ar , A^1 and A^2 are defined above,

with a base in the presence of an alcohol as a solvent, to give the compound of the formula

(III)

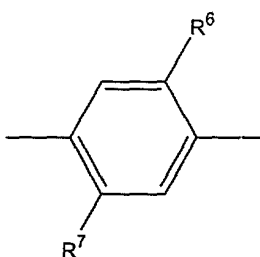


in which Ar, A¹, A², R⁵ and n are as defined above,

- b) warming of the compound of the formula (III) with formation of a polymeric compound of the formula (I),

which comprises employing a secondary or tertiary alcohol having at least 4 carbon atoms as the alcohol in step a).

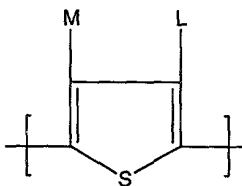
7. The process as claimed in claim 6, wherein Ar in the compounds of the formula (I) is the structural unit



wherein

R⁶ and R⁷ are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 20 carbon atoms, a branched alkyl or alkoxy radical having 1 to 20 carbon atoms, phenyl or benzyl, wherein the above-mentioned radicals are unsubstituted or substituted, halogen, cyano, nitro, or an ester having 1 to 20 carbon atoms.

8. The process as claimed in claim 6, wherein Ar in the compounds of the formula (I) is the structural unit



in which

M and L are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 16 carbon atoms, a branched alkyl or alkoxy radical having 3 to 16 carbon atoms, phenyl or benzyl, where the above-mentioned radicals are unsubstituted or substituted, halogen, cyano, nitro, or an ester having 1 to 16 carbon atoms, or M and L together are a bridge having at least 4 bridge members, which optionally contain one or more heteroatoms.

9. The process as claimed in claim 6, wherein a secondary and/or tertiary alcohol is employed whose boiling point at atmospheric pressure is $<300^{\circ}\text{C}$.
10. The process as claimed in claim 9, wherein the alcohol is s-butanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, 2,3-butanediol, 2-octanol, 3-octanol, 2-methyl-2-hexanol, 2-methyl-3-hexanol, 5-methyl-2-hexanol, cyclohexanol, regio- and stereoisomers of methylcyclohexanol, 1-methylcyclohexanol, t-butanol or 2-phenyl-2-propanol or a mixture thereof.
11. The process as claimed in claim 7, wherein
 R^6 and R^7 are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 20 carbon atoms, a branched alkyl or alkoxy radical having 1 to 20 carbon atoms, phenyl or benzyl, wherein the above-mentioned radicals are unsubstituted or substituted, chlorine, bromine, fluorine, cyano, nitro, or an ester having 1 to 20 carbon atoms.
12. The process as claimed in claim 8, wherein
M and L are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 16 carbon atoms, a branched alkyl or alkoxy radical having 3 to 16 carbon atoms, phenyl or benzyl, where the above-mentioned radicals are unsubstituted or substituted, chlorine, bromine, fluorine, cyano, nitro, or an ester

having 1 to 16 carbon atoms, or M and L together are a bridge having at least 4 bridge members, which optionally contain oxygen, sulfur or oxygen and sulfur.

13. The process as claimed in claim 7, wherein a secondary and/or tertiary alcohol is employed whose boiling point at atmospheric pressure is $<300^{\circ}\text{C}$.
14. The process as claimed in claim 8, wherein a secondary and/or tertiary alcohol is employed whose boiling point at atmospheric pressure is $<300^{\circ}\text{C}$.
15. The process as claimed in claim 7, wherein the alcohol is s-butanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, 2,3-butanediol, 2-octanol, 3-octanol, 2-methyl-2-hexanol, 2-methyl-3-hexanol, 5-methyl-2-hexanol, cyclohexanol, regio- and stereoisomers of methylcyclohexanol, 1-methylcyclohexanol, t-butanol or 2-phenyl-2-propanol or a mixture thereof.
16. The process as claimed in claim 8, wherein the alcohol is s-butanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, 2,3-butanediol, 2-octanol, 3-octanol, 2-methyl-2-hexanol, 2-methyl-3-hexanol, 5-methyl-2-hexanol, cyclohexanol, regio- and stereoisomers of methylcyclohexanol, 1-methylcyclohexanol, t-butanol or 2-phenyl-2-propanol or a mixture thereof.
17. A process as claimed in claim 6, wherein R^6 and R^7 independently of one another are an unbranched alkoxy radical having 1 to 10 carbon atoms, a branched alkoxy radical having 3 to 20 carbon atoms, or phenyl, which is optionally substituted by one or more branched or unbranched alkyl or alkoxy groups having up to 20 carbon atoms.
18. The process as claimed in claim 6, wherein R^5 is n-butyl, i-butyl, s-butyl, t-butyl, i-pentyl, octyl, 3,6,9-trioxadecyl, 2-hydroxyethyl or 2-chloroethyl.
19. The process as claimed in claim 9, wherein R^5 is n-butyl or n-octyl.
20. The process as claimed in claim 10, wherein the alcohol is t-butanol.

21. The process as claimed in claim 5, wherein step b is carried out in the presence of a solvent.
22. The process as claimed in claim 21, wherein said solvent is toluene. - -

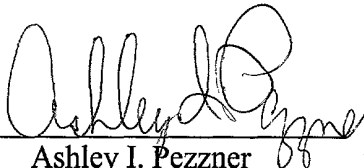
REMARKS

The applicants respectfully request that the preliminary amendment be entered prior to fee calculation and examination. Support for newly added claims 6-16 and 20 can be found in the original claims 1-5. Support for newly added claims 17-19 can be found in the specification at page 5, lines 21-30. Support for newly added claims 21 and 22 can be found in the specification at page 6, lines 26-30. No additional fee is required for the extra claims. If there are any additional fees due in connection with the filing of this response, the Commissioner is authorized to charge or credit any overpayment to Deposit Account No. 03-2775.

A prompt and favorable action is solicited.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

By 
Ashley I. Pezzner
Reg. No. 35,646
Tel. (302) 888-6270

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WO 00/35987

Process for the preparation of derivatives of polyarylenevinylene

Description

- 5 The present invention relates to a process for the preparation of derivatives of polyarylenevinylenes. These conjugated polymers are suitable, inter alia, for electroluminescence applications.

- 10 There is considerable industrial demand for large-area solid-state light sources for a number of applications, predominantly in the area of display elements, display-screen technology and illumination technology. The requirements made of these light sources cannot at present be completely satisfied by any of the existing technologies.

- 15 As an alternative to conventional display and illumination elements, such as incandescent lamps, gas-discharge lamps and non-self-illuminating liquid-crystal display elements, electroluminescent (EL) materials and devices, such as light-emitting diodes (LEDs), have already been in use for some time.

- 20 Besides inorganic electroluminescent materials and devices, low-molecular-weight, organic electroluminescent materials and devices have also been known for about 30 years (see, for example, US-A-3,172,862). Until recently, however, such devices were greatly limited in their practical applicability.

- 25 EP-A-0 423 283 and EP-A-0 443 861 describe electroluminescent devices which contain a film of a conjugated polymer as light-emitting layer (semiconductor layer). Such devices offer numerous advantages, such as
- 30 the possibility of manufacturing large-area, flexible displays simply and inexpensively. In contrast to liquid-crystal displays, electroluminescent displays are self-illuminating and therefore do not require an additional illumination source at the back.

- 35 A typical device in accordance with EP-A-0 423 283 consists of a light-emitting layer in the form of a thin, dense polymer film (semiconductor layer) containing at least one conjugated polymer. A first contact layer is in contact with a first surface, and a second contact layer is in contact with a further surface of the semiconductor layer. The polymer film of the

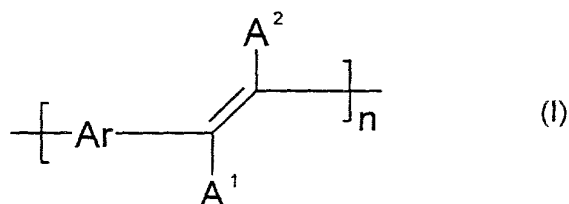
semiconductor layer has a sufficiently low concentration of extrinsic charge carriers so that, on application of an electric field between the two contact layers, charge carriers are introduced into the semiconductor layer, the first contact layer becoming positive compared with the other layer, and the semiconductor layer emits radiation. The polymers used in such devices are conjugated. The term "conjugated polymer" is taken to mean a polymer which has a delocalized electron system along the main chain. The delocalized electron system gives the polymer semiconductor properties and enables it to transport positive and/or negative charge carriers with high mobility.

EP-A-0 423 283 and EP-A-0 443 861 describe poly(p-phenylenevinylene) as polymeric material for the light-emitting layer. This can be modified by alkyl, alkoxy, halogen or nitro substituents on the aromatic ring. Such polymers have since then been investigated in a large number of studies, and dialkoxy-substituted PPVs in particular have already been optimized to a considerable extent toward the market introduction stage (cf., for example, J. Salbeck, Ber. Bunsenges. Phys. Chem. 1996, 100, 1667). However, the development of such polymers can in no way be regarded as complete. Thus, inter alia, improvements are still necessary regarding the service life, stability and also the achievable color. For example, the above polymer class which has been developed the furthest, dialkoxy-PPVs, is only suitable for emission of orange-red light.

The above polymers are only accessible in unsatisfactory yields. Typical polymerizations typically give yields of only 70% of theory, frequently even only less than 50%.

There is therefore a great demand for economical processes for the preparation of polyarylenevinylenes.

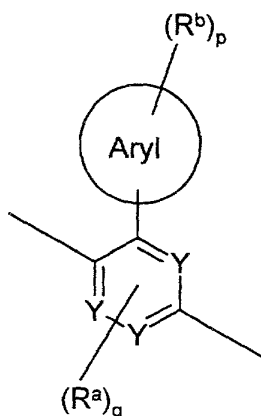
The present invention relates to a process for the preparation of polymers of the formula (I)



in which Ar can adopt the meaning Ar^1 and/or Ar^2 and

Ar^1 is an aromatic ring system having 4 to 20 carbon atoms, which may, if desired, be monosubstituted or polysubstituted by C_1 - C_{20} -alkyl, C_1 - C_{20} -alkoxy, C_3 - C_{20} -branched alkyl, phenyl or benzyl radicals and which may contain up to 4 heteroatoms from the group consisting of oxygen, sulfur and nitrogen in the aromatic ring system,

Ar^2 is a radical of the formula



in which

Y are identical or different and are CH or N;

Aryl is an aryl group having 4 to 14 carbon atoms;

R^a and R^b are identical or different and are a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more non-adjacent CH_2 groups may be replaced by $-O-$, $-S-$, $-CO-$, $-COO-$, $-O-CO-$, $-NR^1-$, $-(NR^2R^3)^+-A^-$, or $-CONR^4-$ and in which one or more H atoms may be replaced by F, or are CN, F, Cl or an aryl group having 4 to 14 carbon atoms, which may be substituted by one or more non-aromatic radicals R^a ;

R^1 , R^2 , R^3 and R^4 are identical or different and are aliphatic or aromatic hydrocarbon radicals having 1 to 20 carbon atoms or are alternatively H;

A^- is a singly charged anion or an equivalent thereof;

q is 0, 1 or 2;

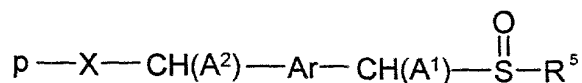
p is 1, 2, 3, 4 or 5;

A^1 and A^2 are identical or different and are hydrogen or a C_1 - to C_{20} -carbon-containing group; and

n is from 5 to 50,000, preferably from 10 to 20,000, in particular from 10 to 15,000;

comprising the following measures:

- 5 a) reaction of at least one monomer of the formula (II)



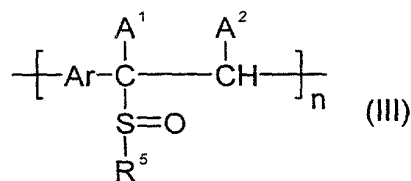
in which

Ar is as defined under the formula (I),

X is a leaving group, and

R⁵ is unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl, such as cyclohexyl, or C₁-C₄-alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, phenyl or benzyl, which may be substituted or unsubstituted and/or contain heteroatoms, such as O, N and Si,

with a base in the presence of an alcohol as solvent, to give the compound of the formula (III)



in which Ar, A¹, A², R⁵ and n are as defined above,

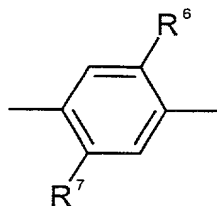
- b) warming of the compound of the formula (III) with formation of a polymeric compound of the formula (I),

- 25 which comprises employing a secondary or tertiary alcohol having at least 4 carbon atoms as the alcohol in measure a).

The radical X is preferably a leaving group, such as halogen, -O-tosylate, -O-mesylate or -O-trifluoroacetate.

In the formula (I), p denotes para in respect of the two methylene radicals -CH₂- on both sides of the radical Ar.

The process according to the invention is preferably used for the preparation of compounds of the formula (I) in which Ar is the structural unit



5

in which

R^6 and R^7 are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 20 carbon atoms, a branched alkyl or alkoxy radical having 1 to 20 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted, halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 20 carbon atoms.

10

15

Particular preference is given to compounds of the formula (I) in which Ar is as defined above, and R^6 and R^7 , independently of one another, are an unbranched alkoxy radical having 1 to 20 carbon atoms, a branched alkoxy radical having 1 to 20 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted, halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 20 carbon atoms.

20

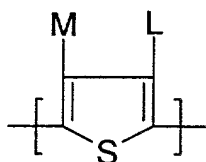
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Preference is furthermore given to compounds of the formula (I) in which R^6 and R^7 , independently of one another, are an unbranched alkoxy radical having 1 to 10 carbon atoms, a branched alkoxy radical having 3 to 20 carbon atoms, or phenyl, which may be substituted by one or more branched or unbranched alkyl or alkoxy groups having up to 20 carbon atoms.

30

R^5 is preferably n-, i-, s- or t-butyl, i-pentyl, octyl, 3,6,9-trioxadecyl, 2-hydroxyethyl or 2-chloroethyl, particularly n-butyl or n-octyl.

The process according to the invention is equally preferably used for the preparation of compounds of the formula (I) in which Ar is the structural unit



in which

M and L are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 16 carbon atoms, a branched alkyl or alkoxy radical having 3 to 16 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted, halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 16 carbon atoms, or M and L together are a bridge having at least 4 bridge members, which may also contain one or more heteroatoms, in particular oxygen and/or sulfur.

The preparation of the monomeric compounds of the formula (II) is described in German Patent Application 19840943.5.

The secondary and/or tertiary alcohols employed in accordance with the invention are, in particular, alcohols having at least 4 carbon atoms whose boiling point at atmospheric pressure is $< 300^{\circ}\text{C}$. Particular preference is given to s-butanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, 2,3-butanediol, 2-octanol, 3-octanol, 2-methyl-2-hexanol, 2-methyl-3-hexanol, 5-methyl-2-hexanol, cyclohexanol, regio- and stereoisomers of methylcyclohexanol, 1-methylcyclohexanol, t-butanol and 2-phenyl-2-propanol, mixtures frequently also being advantageous, in particular if, as in the case of t-butanol, the pure solvent is a solid at room temperature.

Measure b) can be carried out either without solvent, for example in a cast or dried film, or alternatively in a solution, i.e. in the presence of a solvent. The type of this solvent can be selected from the group consisting of inert solvents, such as aromatic solvents, such as chlorobenzene, xylenes and toluene. Toluene has proven particularly suitable. A further group of inert solvents are ethers, for example t-butyl methyl ether and di-n-butyl ether, and cyclic ethers, such as dioxane, tetrahydropyran, tetrahydrofuran and anisole, which are particularly suitable. Also suitable are ketones (acetone, butanone, cyclopentanone and cyclohexanone), sulfones (DMSO), nitriles (acetonitrile and benzonitrile), esters (butyl

acetate and methyl benzoate), lactones (butyrolactone), amides (DMF and N-methylformamide) and lactams (NMP and N-methylcaprolactam).

5 Solvents having various functionalities, such as ethyl cyanoacetate and 2-methoxyethyl acetate, can also advantageously be used.

Preference is also given to the specific alcohols listed under measure a). Even polar, protic solvents, such as n-butanol, n-propanol, ethanol, methanol and water, can advantageously be employed.

10

Mixtures of the abovementioned solvents can frequently also advantageously be used, particular preference being given to homogeneously miscible solvents. In an economically particularly attractive embodiment, measure b) is carried out in situ, i.e. in the same solvent in which measure a) is also carried out, it being possible, if desired, for the concentration to be modified by evaporation or dilution.

15

The pressure during both reaction steps is of secondary importance and depends especially on the vapor pressure of the solvent at the selected temperature.

20

In measures a) and b), the exclusion of oxygen is ensured by flushing with an inert gas, such as nitrogen or argon.

25

Suitable bases for measure a) are inorganic and organic bases. Suitable inorganic bases are NaOH, KOH and LiOH. Suitable organic bases are sterically hindered bases, such as lithium diisopropylamide (LDA), sodium trimethylsilanoate, bis(trimethylsilyl)potassium amide, but in particular alkali metal tert-butoxides, such as KOtBu, NaOtBu and the Na and K alkoxides of the alcohols used as solvent. Commercially available NaOtBu gives particularly good results.

30

The amount of base employed can vary greatly, it being possible to employ up to 8 equivalents of base per mole of monomer of the formula (II). However, it is preferred to employ from 0.85 to 1.6 equivalents of base, in particular from 0.95 to 1.05 equivalents, per mole of monomer of the formula (II). This ratio proves to be particularly advantageous since the excess amount of base can in part only be removed from the final product with considerable effort.

35

The reaction temperatures and times for measure b) can be varied over a broad range, with a higher temperature generally being selected for a shorter reaction time. At temperatures of up to +200°C, the reaction times should be selected between 5 minutes and 48 hours. Preference is given to temperatures above 60°C, the reaction particularly preferably being carried out at the boiling point of the solvent used.

With the aid of the process according to the invention, the yields of compounds of the formula (I), based on the monomer of the formula (II) employed, are significantly increased and are more than 80%, preferably even more than 85% of theory.

Examples

All reactions were carried out under nitrogen.

Molecular weights were determined by gel permeation chromatography (GPC) in THF against polystyrene standard (PS).

Example 1

Polymerization of 4-(octylsulfinylmethyl)-3-methoxy-6-(3,7-dimethyloctyloxy)-benzyl chloride and 4-(octylsulfinylmethyl)-6-methoxy-3-(3,7-dimethyloctyloxy)benzyl chloride to give a precursor polymer

2 mmol of the monomer in 14 ml of s-butanol were degassed by passing a stream of nitrogen through for one hour. A solution or suspension of sodium t-butoxide (0.25 g, 2.6 mmol) in 6 ml of s-butanol was added in one portion. One hour later, the reaction solution was added dropwise with vigorous stirring to 200 ml of ice-water. The mixture was neutralized using 1N hydrochloric acid and extracted three times with 100 ml of chloroform each time. After concentration under reduced pressure, the crude product was taken up in 12.5 g of chloroform, and the solution was added dropwise to 125 g of a precipitant, i.e. a mixture of *n*-hexane and diethyl ether (1:1, w/w). The precipitated precursor polymer was filtered off with suction, rinsed with the precipitant and dried under reduced pressure.

The yield was virtually quantitative.

GPC: $\overline{M}_w = 307,000$, polydispersity 2.1

Conversion of the precursor polymer:

Poly[2-methoxy-5-(3,7-dimethyloctyloxy)phenylene-1,4-vinylene-co-5-methoxy-2-(3,7-dimethyloctyloxy)phenylene-1,4-vinylene]

- The precursor polymer was refluxed for 3 hours in 50 ml of toluene (110°C).
 5 After precipitation in 300 ml of methanol, 3.6 g of the conjugated polymer were obtained. Yield 98%, based on the monomer employed in Example 1.
 GPC: $\overline{M}_w = 560,000$, polydispersity 3.8

Comparative Example 1

- 10 2 g (4.6 mmol) of a 1:1 mixture of the isomers α -chloro- α' -n-butylsulfinyl-2-(3,7-dimethyloctyloxy)-5-methoxy-*p*-xylene and α -chloro- α' -n-butylsulfinyl-2-methoxy-5-(3,7-dimethyloctyloxy)-*p*-xylene were dissolved in 25 ml of NMP, and the solution was flushed with nitrogen for one hour. 0.468 g (4.87 mmol, 1.05 eq.) of NaOtBu was dissolved in 20 ml of *s*-BuOH, and the solution was
 15 flushed with nitrogen for one hour. The NaOtBu solution was added at 23°C to the solution of the monomer. One hour later, the mixture was added to 100 ml of H₂O and neutralized using 0.1N HCl. The aqueous phase was extracted with 100 ml of chloroform. The organic phase was dried over MgSO₄ and evaporated under reduced pressure, giving 0.36 g of the crude,
 20 intense yellow precursor polymer.

Conversion of the precursor polymer

- Heating in 50 ml of boiling toluene (110°C, 3 hours) and precipitation in 300 ml of methanol gave 0.28 g (14 %) of the conjugated polymer.
 25 GPC: $\overline{M}_w = 654,000$, PD = 5.3.

Example 2

- 7 g (0.0162 mol) of a 1:1 mixture of the isomers α -chloro- α' -n-butylsulfinyl-2-(3,7-dimethyloctyloxy)-5-methoxy-*p*-xylene and α -chloro- α' -n-butylsulfinyl-2-methoxy-5-(3,7-dimethyloctyloxy)-*p*-xylene were dissolved in 60 ml of
 30 *s*-BuOH in a 250 ml three-necked flask and flushed with nitrogen. A likewise oxygen-free solution of 2.04 g of NaOtBu (0.0214 mol) in 60 ml of *s*-BuOH was added to the solution at 23°C, and, after one hour, the solution was added dropwise to 300 ml of H₂O. After neutralization using 0.1N HCl, the
 35 aqueous phase was extracted with 200 ml of chloroform. The organic phase was concentrated over MgSO₄ under reduced pressure, giving 6 g (0.0151 mmol = 93 %) of the precursor polymer.
 GPC: $M_p = 2.18 \times 10^5$; $\overline{M}_w = 3.07 \times 10^5$; $\overline{M}_n = 1.47 \times 10^5$; PD = 2.08.

Conversion of the precursor polymer

Treatment for 3 hours in 50 ml of boiling toluene (110°C) and precipitation in 300 ml of methanol gave 3.9 g (0.0135 mol = 83 %) of the conjugated polymer.

- 5 GPC: $M_p = 4.42 \times 10^5$; $\overline{M}_w = 5.60 \times 10^5$; $\overline{M}_n = 1.47 \times 10^5$; $D = 3.80$.

Examples 3 – 5 and Comparative Examples 2 – 11

Polymerization of α -chloro- α' -octylsulfinyl-*p*-xylene

- 10 2 mmol of the monomer were dissolved in 14 ml of a solvent and degassed by passing nitrogen through for one hour. A solution or suspension, likewise degassed at 30°C, of sodium *t*-butoxide (0.25 g, 2.6 mmol) in 6 ml of the same solvent was added in one portion at 30°C. One hour later, the reaction mixture was added dropwise to 200 ml of ice-water with vigorous stirring. The mixture was neutralized using 1N hydrochloric acid and extracted three times
15 with 100 ml of chloroform each time. After concentration under reduced pressure, the crude product was taken up in 12.5 g of chloroform, and the solution was added dropwise to 125 g of a precipitant, i.e. a mixture of *n*-hexane and diethyl ether (1:1, w/w). The precipitated precursor polymer was filtered off with suction, rinsed with the precipitant and dried under
20 reduced pressure.

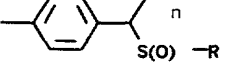
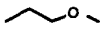
| Example | Solvent | Yield of precursor polymer (%) | Non-polymeric products (%) | $\overline{M}_w (\times 10^3)$ | PD |
|---------|---------------------------------|--------------------------------|----------------------------|--------------------------------|-----|
| Comp. 2 | CH ₂ Cl ₂ | 76 | 12 | 350 | 2.4 |
| Comp. 3 | THF | 81 | 12 | 735 | 3.9 |
| Comp. 4 | DMSO | 49 | 41 | 475 | 4.0 |
| Comp. 5 | MMF | 28 | 69 | 780 | 3.0 |
| Ex. 3 | <i>s</i> -BuOH | 88 | 8 | 238 | 2.0 |

MMF = monomethylformamide

| Example | Solvent | Yield of precursor polymer (%) | Non-polymeric products (%) | $\bar{M}_w (x 10^3)$ | PD |
|----------|------------------|--------------------------------|----------------------------|----------------------|-----|
| Comp. 6 | MeOH | 0 | 100 | -- | -- |
| Comp. 7 | EtOH | 11 | 87 | 104 | 1.7 |
| Comp. 8 | <i>n</i> -PrOH | 30 | 62 | 118 | 1.7 |
| Comp. 9 | <i>n</i> -BuOH | 28 | 65 | 104 | 1.7 |
| Comp. 10 | <i>n</i> -PentOH | 42 | 56 | 84 | 1.7 |
| Comp. 11 | <i>i</i> -PrOH | 21 | 78 | 437 | 2.3 |
| Ex. 4 | <i>t</i> -BuOH | 89 | 4 | 225 | 2.1 |
| Ex. 5 | <i>s</i> -PentOH | 89 | 5 | 296 | 2.4 |

Examples 6 – 12

5 Polymerization of various α -chloro- α' -alkylsulfinyl-*p*-xylenes in *s*-butanol under the conditions as in Example 3

| |  | Precursor polymer yield (%) | $\bar{M}_w (x 10^3)$ | PD |
|------------|---|-----------------------------|----------------------|-----|
| Example 6 | R = <i>n</i> -butyl | 82 | 540 | 2.5 |
| Example 7 | R = <i>n</i> -octyl | 88 | 238 | 2.0 |
| Example 8 | R = <i>i</i> -butyl | 82 | 280 | 2.2 |
| Example 9 | R = <i>i</i> -pentyl | 83 | 500 | 2.3 |
| Example 10 | R = <i>s</i> -Bu | 78 | 260 | 2.2 |
| Example 11 | R = <i>t</i> -Bu | 77 | 42 | 1.9 |
| Example 12 | 5  | > 49 ^{b)} | 435 | 2.2 |

b) Yield: 80 % before precipitation. Figure relates to isolated polymer. Residues are in the liquor.

Examples 13 – 14 and Comparative Examples 12 – 15

Polymerization of α -chloro- α' -n-butylsulfinyl-2,5-dimethyl-*p*-xylene under the conditions as in Example 3

5

| | Solvent | T (°C) | Eq. of base | $\bar{O}_w (x 10^3)$ | PD | Yield (%) |
|----------|---|-----------|----------------|----------------------|-----|--------------|
| Comp. 12 | Monomethylformamide (MMF) | 20 | 1.3 | 620 | 2.9 | 25 |
| Comp. 13 | MMF : CH ₂ Cl ₂ (3:2) | 20 | 1.3 | 632 | 2.6 | 25 |
| Comp. 14 | Formamide : THF (3:1) | 20 | 1.3 | 390 | 2.4 | 20 |
| Comp. 15 | NMP | -10 | 1.3 | 192 | 1.9 | 55 |
| Ex. 13 | <i>t</i> -Butanol | 20 | 1.3 | 177 | 1.9 | 85 |
| Ex. 14 | <i>s</i> -Butanol | 20 | 1.3 | 773 | 2.6 | 90 |

Example 15 and Comparative Examples 16 – 17

Polymerization of α -chloro- α' -n-butylsulfinyl-2,5-dimethoxy-*p*-xylene under the conditions as in Example 3

10

| | Solvent | T (°C) | Eq. of base | $\bar{O}_w (x 10^3)$ | PD | Yield (%) |
|----------|-------------------|-----------|----------------|----------------------|-----|--------------|
| Comp. 16 | MMF | 20 | 1.3 | 267 | 1.8 | 35 |
| Comp. 17 | NMP | -10 | 1.3 | 90 | 1.7 | 30 |
| Ex. 15 | <i>s</i> -Butanol | 20 | 1.3 | 133 | 1.9 | 75 |

Example 16

Polymerization of α -chloro- α' -n-butylsulfinyl-2,5-chloro-*p*-xylene under the conditions as in Example 3

15

At $T = 20^{\circ}\text{C}$, 65% of the corresponding precursor polymer with 1.3 base equivalents were obtained, having an M_w of 678,000 g/mol in GPC and a PD of 3.3.

5 Example 17

Polymerization of α -chloro- α' -butylsulfinyl-*p*-xylene

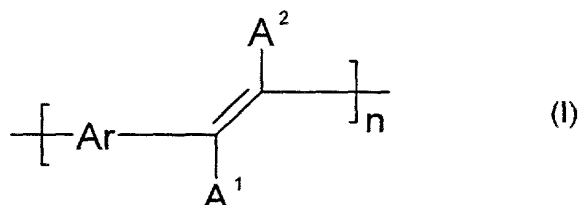
- 10.2 g (0.106 mol) of NaOtBu dissolved in 240 ml of *s*-butanol were poured in one portion into a mechanically stirred solution of 20 g (0.082 mol) of α -chloro- α' -butylsulfinyl-*p*-xylene in 570 ml of *s*-butanol. After stirring for a further 60 minutes, the mixture was poured into 1.5 l of ice-water, neutralized using 1N HCl and extracted with CHCl_3 . The latter was distilled off under reduced pressure, the residue was taken up in CHCl_3 , and the product was precipitated in diethyl ether.
- 15 The white solid dried under reduced pressure gave 14.7 g (86 %) of precursor polymer.

A storage experiment in the freezer at -18°C showed no discoloration, no weight change and no odor nuisance.

Patent claims

HOE 98/F 135

1. A process for the preparation of polymers of the formula (I)



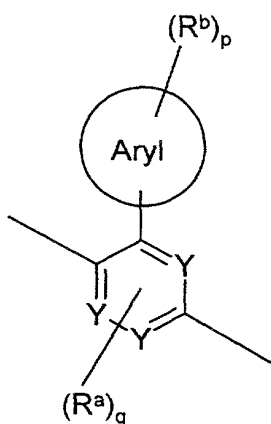
5

in which Ar can adopt the meaning Ar^1 and/or Ar^2 and

Ar^1 is an aromatic ring system having 4 to 20 carbon atoms, which may, if desired, be monosubstituted or polysubstituted by C_1 - C_{20} -alkyl, C_1 - C_{20} -alkoxy, C_3 - C_{20} -branched alkyl, phenyl or benzyl radicals and which may contain up to 4 heteroatoms from the group consisting of oxygen, sulfur and nitrogen in the aromatic ring system,

10

Ar^2 is a radical of the formula



15

in which

Y are identical or different and are CH or N;

Aryl is an aryl group having 4 to 14 carbon atoms;

- 20 R^a and R^b are identical or different and are a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more non-adjacent CH_2 groups may be replaced by $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{COO}-$, $-\text{O}-\text{CO}-$, $-\text{NR}^1-$, $-(\text{NR}^2\text{R}^3)^+-\text{A}^-$, or $-\text{CONR}^4-$ and in which one or more H atoms may be replaced by F, or are CN, F, Cl

or an aryl group having 4 to 14 carbon atoms, which may be substituted by one or more non-aromatic radicals R^a ;

R^1 , R^2 , R^3 and R^4 are identical or different and are aliphatic or aromatic hydrocarbon radicals having 1 to 20 carbon atoms or are alternatively H;

A^- is a singly charged anion or an equivalent thereof;

q is 0, 1 or 2;

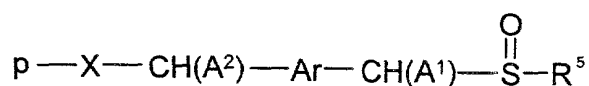
p is 1, 2, 3, 4 or 5;

A^1 and A^2 are identical or different and are hydrogen or a C_1 - to C_{20} -carbon-containing group; and

n is from 5 to 50,000;

comprising the following measures:

a) reaction of at least one monomer of the formula (II)



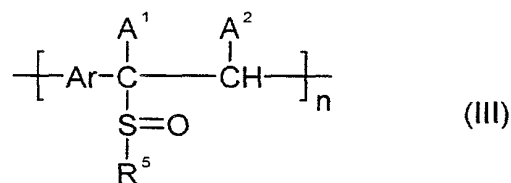
in which

Ar is as defined under the formula (I),

X is a leaving group, and

R^5 is unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl or C_1 - C_4 -alkyl-substituted cyclic alkyl, which may be substituted or unsubstituted and/or contain heteroatoms, such as O, N and Si,

with a base in the presence of an alcohol as solvent, to give the compound of the formula (III)

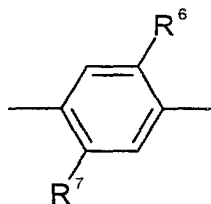


in which Ar, A^1 , A^2 , R^5 and n are as defined above,

b) warming of the compound of the formula (III) with formation of a polymeric compound of the formula (I),

which comprises employing a secondary or tertiary alcohol having at least 4 carbon atoms as the alcohol in measure a).

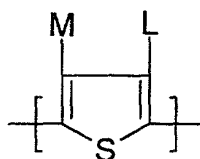
2. The process as claimed in claim 1, wherein the compounds of the formula (I) are those in which Ar is the structural unit



in which

R^6 and R^7 are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 20 carbon atoms, a branched alkyl or alkoxy radical having 1 to 20 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted, halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 20 carbon atoms.

3. The process as claimed in claim 1, wherein the compounds of the formula (I) are those in which Ar is the structural unit



in which

M and L are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 16 carbon atoms, a branched alkyl or alkoxy radical having 3 to 16 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted, halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 16 carbon atoms, or M and L together are a bridge having at least 4 bridge members, which may also contain one or more heteroatoms, in particular oxygen and/or sulfur.

4. The process as claimed in one of claims 1 to 3, wherein a secondary and/or tertiary alcohol is employed whose boiling point at atmospheric pressure is $< 300^{\circ}\text{C}$.

5. The process as claimed in claim 4, wherein the alcohol employed is s-butanol, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, 2-methyl-2-butanol, 2,3-butanediol, 2-octanol, 3-octanol, 2-methyl-2-hexanol, 2-methyl-3-hexanol, 5-methyl-2-hexanol, cyclohexanol, regio- and stereoisomers of methylcyclohexanol, 1-methylcyclohexanol, t-butanol or 2-phenyl-2-propanol, or a mixture thereof.

0986312.073001

Abstract

Process for the preparation of derivatives of polyarylenevinylene

- 5 The present invention relates to a selected process for the preparation of polyarylenevinylenes. These conjugated polymers are suitable for electroluminescence applications.

09868312.073001



1998/F135 US PCT

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Process for the preparation of derivatives of polyarylenevinylene

the specification of which

- is attached hereto

- was filed on November 17, 1999 as International Patent Application PCT/EP99/08830 and including all the amendments through the date hereof.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) for which Priority is Claimed:

Federal Republic of Germany, 19857661.7 of December 15, 1998

And I hereby appoint

Rudolf E. Hutz, Reg.No. 22,397; Harold Pezzner, Reg.No. 22,112; Richard M. Beck, Reg.No. 22,580; Paul E. Crawford, Reg.No. 24,397; Thomas M Meshbesh, Reg.No. 25,083; Robert G. McMorro, Jr., Reg.No. 30,962; Patricia Smink Rogowski, Reg.No. 33,791; Ashley I. Pezzner, Reg.No. 35,646; William E. McShane, Reg. 32,707; James T. Moore, Reg. No. 35,619; Mary W. Bourke, Reg.No. 30,982; Gerard M. O'Rourke, Reg.No. 39,794; Christine M. Hansen, Reg.No. 40,634; Allan N. Kutzenco, Reg. No. 38,945; James M. Olsen, Reg.No. 40,408; Francis DiGiovanni, Reg.No. 37,310; Frank Z. Yang, Reg. No. 35,417; Eric J. Vain, Reg.No. 42,517; Daniel C. Mulveny, Reg.No. P-45,897; and Elliot C. Mendelson, Reg.No. 42,878 all of CONNOLLY AND HUTZ, P.O.Box 2207, Wilmington, Delaware 19899-2007, my attorneys with full power of substitution, to prosecute this application, and transact all business in the Patent and Trademark Office connected therewith and I hereby request that all correspondence in this application be directed to:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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